



Direct stable isotope porewater equilibration and identification of groundwater processes in heterogeneous sedimentary rock

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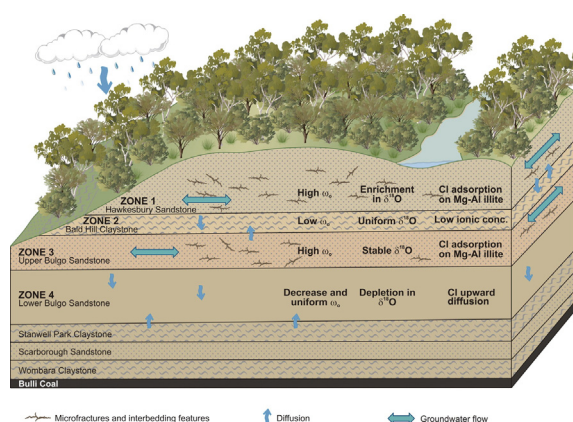
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HIGHLIGHTS

- Multidisciplinary approaches used to resolve groundwater movement in sedimentary basin
- First application of core pore water ICOS analysis for stable isotopes in Sydney Basin
- Four distinct hydrogeological zones were identified.
- Chloride concentration is associated with cement/matrix water interaction.
- Important for groundwater management of sensitive ecosystems

GRAPHICAL ABSTRACT



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ABSTRACT

The off-axis integrated cavity output spectrometry (ICOS) method to analyse porewater isotopic composition has been successfully applied over the last decade in groundwater studies. This paper applies the off-axis ICOS method to analyse the porewater isotopic composition, attempts to use the isotopic shift in groundwater values along with simple geochemical mixing model to define the groundwater processes in the Sydney Basin, Australia. Complementary data included geophysical, hydrogeological, geochemical, and mineralogical investigations. Porewater from core samples were analysed for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ from various sedimentary units in the Basin and compared to endpoint water members. Stable $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of porewaters in the Basin (-9.5 to 2.8‰ for $\delta^{18}\text{O}$ and -41.9 to 7.9‰ for $\delta^2\text{H}$) covered a relatively narrow range in values. The variability in water isotopes reflects the variability of the input signal, which is the synoptic variability in isotopic composition of rainfall, and to a minor extent the subsequent evaporation. The porosity, bulk density and mineralogy data demonstrate the heterogeneity that adds the complexity to variations in the isotope profile with depth. The source of chloride in the sedimentary sequence was related to rock–water and cement/matrix–water interaction rather than to evaporation. The heterogeneous character of the sedimentary rock strata was supported by a change in pore pressures between units, density and variability in rock geochemical analyses obtained by using X-ray fluorescence (XRF) and X-ray power diffraction analyses. This research identified distinct hydrogeological zones in the Basin that

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were not previously defined by classic hydrogeological investigations. Isotopic signature of porewaters along the detailed vertical profile in combination with mineralogical, geochemical, geophysical and hydrogeological methods can provide useful information on groundwater movement in deep sedimentary environments. The findings of the study are valuable in management of sensitive ecosystems and potable resources above mining areas.

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1. Introduction

Understanding the characteristics and presence of low permeability strata within sedimentary basins is important to define groundwater flow in basins and to determine their ability to protect potable water resources and associated ecosystems. This is particularly important in the southern Sydney Basin where six underground coal mines currently operate within the Sydney water supply catchment area and underneath wetlands and sensitive ecosystems. Although the geology of the Sydney Basin is well-defined (Ashley and Duncan, 1977; Rust and Jones, 1987; Sherwin and Holmes, 1986), no systematic aquifer system analysis has been undertaken in the southern part of the Basin (McKibbin and Smith, 2000; Lee, 2000).

It is widely accepted that, on a regional scale lateral groundwater flow is dominated by thick sandstone units while vertical flow is dominated within the low hydraulic conductivity (K) units (Parsons Brinckerhoff, PB, 2011; SCSG, 2006). Furthermore, groundwater models developed for underground mining projects in these sedimentary strata assume that the low K claystone units provide a hydraulic barrier between aquifers above and below this unit and do not consider the effects of small scale heterogeneities (<2 m thickness) on flow (GHD, 2007; Nicol et al., 2014; RPS, 2014). This research tests the hypothesis that stable isotopes of water can identify groundwater processes in heterogeneous sedimentary rock when combined with other investigative methods. A number of sub-hypotheses were tested as part of this broad research objective. Although this is the first time that porewater stable isotope method has been applied in the Sydney Basin, the stable isotopes of groundwater have been measured previously. The application of the stable isotopes of groundwater had an important role in the Sydney Basin in characterising groundwater chemistry for urban water supply evaluation (KBR, 2008), sustainable management of stressed groundwater systems and conservation of groundwater dependent ecosystems (McLean et al., 2007) and assessment of the value of groundwater resources in the area targeted by coal seam gas extraction (AGL, 2013; Bartrop, 2014).

The use of water-vapour equilibration method to measure stable isotopes on porewaters is well-documented in recent literature (Hendry and Wassenaar, 2009; Hendry et al., 2011; Hendry et al., 2013; Garvelmann et al., 2012). This method allows characterisation of detailed vertical profiles by measurement of porewater stable isotopes using core samples. The technique had not yet been used for heterogeneous sedimentary rock, in environments important for water supply and mining.

Another advantage of this technique is that it allows the collection of sample where otherwise this would not be possible. Due to the thickness of the sediments within the basin (>300 m), ground movement as a result of subsidence and microseismic activity (longwall mining induced), it is impractical to install standpipe piezometers and thus difficult to obtain representative groundwater sample using classic groundwater techniques (Stuckey and Mulvey, 2013) to provide detailed understanding of the vertical profile. The knowledge of the modern-day rainfall isotopic composition in the Sydney Basin (Hughes and Crawford, 2013) allows the interpretation of porewater data. The study by Crawford et al. (2013) found that $\delta^{18}\text{O}$ value and its variability was dependent on the prevailing weather system and that the large scale rainout during transport had more influence on the $\delta^{18}\text{O}$ than different moisture sources. Rainfall in the Sydney Basin that is sourced

from east coast low ECL system has been found to have more depleted arithmetic mean precipitation $\delta^{18}\text{O}$, shows largest variability in $\delta^{18}\text{O}$ (−4‰ to −26‰ and standard deviation 5.6‰) and deuterium excess (D-excess) compared to other systems, in particular the inland western trough. Both the isotopic composition ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) and the D-excess of precipitation therefore represent an isotopic signal which is influenced by long term climate and weather system conditions (ECL and western trough representing the end points). Given that very little climate change occurred over the last 6 ka, it is considered that the historical precipitation is similar to current. These weather systems have the primary influence on the porewater composition and could provide information on paleoclimate and ultimately groundwater processes. Secondary influence is due to strata heterogeneity and evaporation. Therefore, the objective of this research was to use direct porewater isotope measurements (along vertical profile) on core samples supported by detailed mineralogical analysis using XRF and XRD analyses, complemented by geophysical downhole logging, pore pressure analysis, porosity, chloride concentration (measured directly on samples) and simple geochemical mixing model to understand groundwater flow processes in a thick heterogeneous sedimentary sequence. This is the first study to use the direct stable isotope analysis on rock core samples interpreted in the context of heterogeneous bedded strata (hard rock Permo-Triassic). The major outcome of the study is that the porewater isotopes can prove useful, in areas where no recent glaciation has occurred but where input rainfall characteristics are thoroughly investigated, and where data is supported by other groundwater investigation methods. The study has also enabled hydrogeological zones to be defined for the first time in the Sydney Basin based on stable isotope analysis on rock cores, taking into consideration flow and mass transport directions. The findings of this study can assist with management of ecosystems and wetlands in the areas underlain by longwall coal mines.

2. Geology and hydrogeology

2.1. Geology

The study area is located on the Illawarra plateau in the southern part of the Sydney Basin, approximately 15 km from the Pacific Ocean and at an elevation of about 340 m above sea level (a.s.l.). The outcropping rocks within this part of the Basin are mainly of Triassic age with minor Permian age rocks exposed along the coastal areas and at the escarpment (Fig. 1).

The Permian strata were deposited during the relatively quiet period within alluvial and estuarine environments and are therefore rich with coal resources (Table 1). The Triassic sequence overlies the Permian strata and comprises early Triassic Narrabeen Group sediments and mid-Triassic Hawkesbury Sandstone.

The major lineaments, joints and faults within the Basin have similar orientation (Cook and Johnson, 1970) and generally do not represent a conduit for groundwater flow. The reason for this is the presence of clayey infill, high horizontal stresses perpendicular to the extent of the fault and limited vertical extent (Tonkin and Timms, 2015). Sedimentary strata dip at a low angle and almost horizontally to the north-northeast (Sherwin and Holmes, 1986). Based on the depositional environment and structural compression, the stratigraphy encountered in

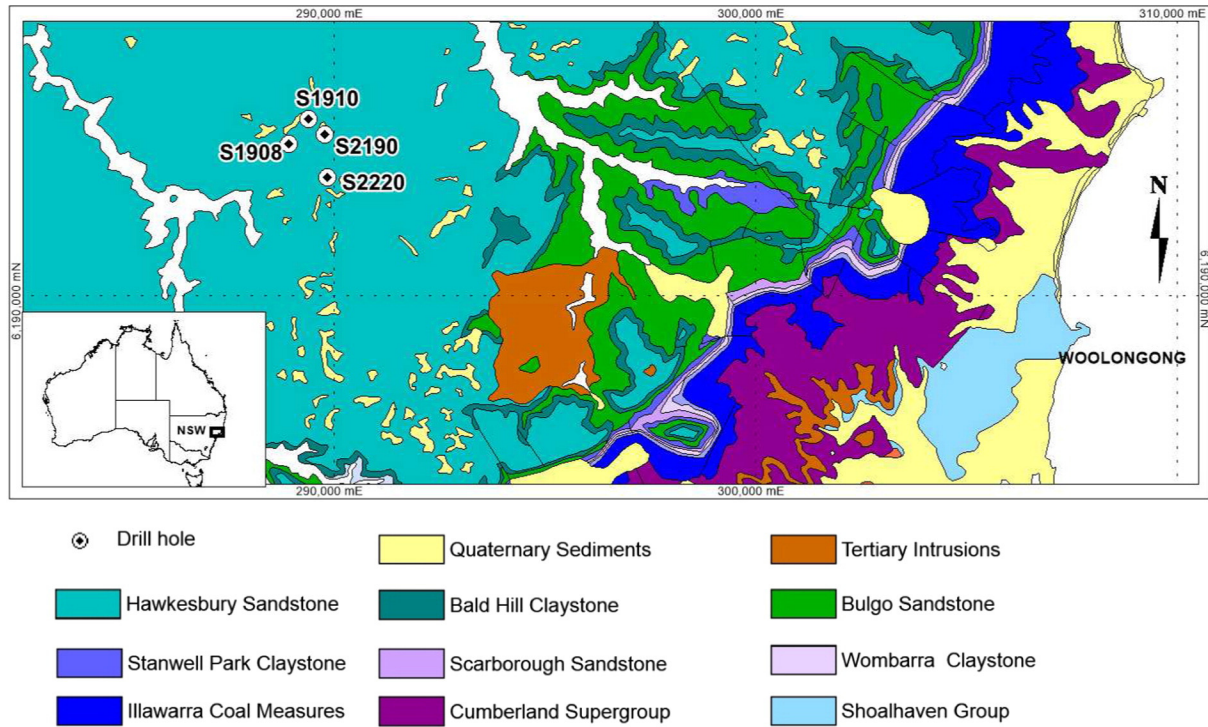


Fig. 1. Geology map (after Geological Survey, NSW, 1999).

drillhole S2220 in this study is considered typical of the southern Sydney Basin (Table 1, Fig. 1).

Triassic deposition occurred mainly in alluvial and deltaic environments. The deposition started with the Narrabeen Group sediments that outcrop at the escarpment and comprise two sandstone and three claystone intervals (Sherwin and Holmes, 1986).

Bulgo Sandstone (BGSS) is the thickest unit in the Narrabeen Group (about 150 m) and comprises massive bedded sandstone with up to

10 m thick siltstone and claystone (comprising mainly illite and to a minor extent kaolinite). Where sandstone pores are filled with illite, kaolinite, chlorite, clay–limonite (Ward, 1970, 1980; Bowman, 1974) and iron oxides the porosity will be significantly reduced. The exception is the iron oxide coating of siderite, or clay coating of quartz that inhibits its growth and therefore preserves the primary porosity (Al Gahtani, 2013). An increase in porosity can result from dissolution of carbonate cement within pores.

Table 1
Stratigraphy of the south Sydney Basin.

Stratigraphy	Group	Subgroup	Formation	Description	Thickness (m)
Quaternary			Alluvium	Quartz and lithic sand, silt and clay	
			Hawkesbury Sandstone	Massive or thickly bedded quartzose sandstone with siltstone, claystone and shale lenses up to several meters thick (Alder et al, 1991)	<275
Triassic	Narrabeen Group	Gosford	Newport	Fine grained sandstones interbedded with fine grained sandstones, siltstones and claystones	<91
			Garie	Clay-pellet kaoline rock	<3
			Bald Hill Claystone	Massive chocolate-coloured claystone	<20
		Clifton	Bulgo Sandstone	Thickly bedded sandstone with siltstone and claystone bands (<3 m), conglomerate towards the base (Sherwin and Holmes, 1986)	100
			Stanwell Park Claystone	Claystone and sandstone intervals, with few conglomeritic beds	50
			Scarborough Sandstone	Coarse lithic sandstone and conglomerate	24
			Wombarra Claystone	greenish grey to chocolate claystones and sandstones	0–30
Permian	Illawarra Coal Measures	Sydney	Bulli Coal	Coal interbedded with shale,	3
			Eckersley Formation	carbonaceous claystone,	8–120
			Wongawilly Coal	claystone, tuff, and sandstone	3–9

Bald Hill Claystone (BHCS) is the most extensive claystone unit within the Narrabeen Group and is made up of kaolinite, haematite and siderite (Bunny and Herbert, 1971). These claystone beds are massive and siderite nodules are common. The Garie Formation (2 m thickness) which overlays BHCS also consists of clay-pellet kaolin however with an absence of haematite compared to BHCS. Newport Formation overlies the Garie Formation and comprises mainly sandstone with minor siltstone and claystone (Dickson, 1972).

The boundary between Narrabeen Group and HBSS is characterised by a hiatus of sedimentary deposition. The HBSS unit outcrops over the study area and forms the cliffline on the Illawarra Escarpment. It comprises 95% quartzose sandstone with minor siltstone and claystone interbeds that occur mostly as lenses in the upper part of the unit (Bowman, 1974). The matrix is argillaceous and secondary quartz-siderite cement is present. Bowman (1974) considered that sandstone matrix is mostly made up of illite and to a lesser extent of kaolinite. Iron oxide is found as coating on the detrital grains (Zaid and Al Gahtani, 2015).

With reference to the S2220 borehole in this study, the Stanwell Park Claystone (SPCS) is the lowermost unit and HBSS is the uppermost unit (Table 1).

2.2. Regional hydrogeology

There is no unique conceptual hydrogeological model for the southern Sydney Basin, despite extensive datasets and numerous groundwater studies including: bore records (NSW Office of Water database) on groundwater yields from porous HBSS (Woolley, 1991); water supply studies in the Upper Nepean (SCA, 2005); groundwater investigations for coal seam gas and coal mining; and several public reports discussing particular hydrostratigraphic units (Ward and Kelly, 2013; AGL, 2011). Most hydrogeological classifications are based on localised regions and mine site specific investigations. In general two hydrostratigraphic units are defined above SPCS: the HBSS, and the Narrabeen Group.

The HBSS (Fig. 1) is classified as an aquifer with three units (Lee, 2000): upper and lower characterised by higher hydraulic conductivity (K_H) and quartzose sandstone and middle unit characterised by lower K_H and clayey sandstones and shales. The total thickness of the HBSS is over 200 m regionally. The permeability of this aquifer is influenced by primary and secondary porosity, with primarily horizontal along the bedding planes and regionally related to topography (McKibbin and Smith, 2000). In general, the standing water levels in this unit are within 30 m from surface, however this varies with topography (Merrick, 2008). KBR (2008) report that the age of groundwater for HBSS ranges from 3000–6000 years (based on ^{14}C radiocarbon dating).

The Narrabeen Group includes both aquifers and aquitards. This system is confined and pressurised, except where it outcrops. Within this group, the Newport Formation, BGSS and Scarborough Sandstone are considered aquifers, and the Garie Formation, BHCS and SPCS are considered aquitards (AGL, 2013; Broadstock, 2011; GHD, 2007; PB, 2011; SCA, 2005). The units classified as aquifers also contain thin claystone, fine-grained sandstone and siltstone layers of various thicknesses and their heterogeneity is recognised (Pells, 1993). The regional groundwater flow in the Narrabeen Group is to the north-northeast.

BHCS is characterised as an aquitard (SCA, 2005; AGL, 2013) although the geometric mean of horizontal permeability values (recorded from a number of packer tests) is an order of magnitude higher than that for HBSS (Pells, 1993). The BGSS underlays BHCS and although it is described as massive unit, petrological analysis of samples indicates that it is diverse (Pells, 1993). Due to presence of numerous low permeability units of different thickness within the Narrabeen Group both regionally and locally, overall the yield in this group is lower and water quality is poorer compared to HBSS.

3. Methods and experimental design

A 289 m deep hole (S2220) was drilled (about 20 km south of Wilton, NSW, Fig. 1) through the HBSS, and a near complete sequence of the Narrabeen Group including the top of SPCS, with coal at around 360 m. The drilling was undertaken by diamond drilling method using 3 m long double barrel (60 mm inside diameter). The drilling fluid was fresh water sourced from the nearby reservoir and drilling additives were not required. Deuterium oxide 99.9% was added to drilling water on one occasion (250 mL to 17,000 L of water) during drilling to determine whether or not drilling water was seeping into the core. Possible porewater contamination was checked by analysing drilling water and core samples (porewater) after the addition of deuterium oxide. If the porewater indicates $\delta^2\text{H}$ enrichment, it can be suspected that contamination is occurring from drilling water.

After the drill core was extracted from the ground, the core was photographed and wiped to remove drilling fluids. Core samples (60 mm in diameter and 5 to 10 cm in length) were vacuum-packed immediately in tough plastic bags and placed in a chilled storage box. The core samples were collected every 3 m, and the analysis undertaken within 10 days of drilling being completed on every second sample (6 m) and the infill samples were analysed after 2 months (total of 71 rock core samples). In addition, surface water from the nearby stream, a coal seam water sample and four drilling water samples spiked with deuterium oxide were analysed for $\delta^{18}\text{O}$ and $\delta^2\text{H}$.

3.1. Off-axis ICOS analysis

The core samples were analysed for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ using $\text{H}_2\text{O}_{(\text{water})}$ – $\text{H}_2\text{O}_{(\text{vapour})}$ porewater equilibration (Wassenaar et al., 2008) and off-axis ICOS using Los Gatos (LGR) water vapour analyser (WVIA RMT-EP model 911-0004). The samples were prepared based on the method described by Wassenaar et al. (2008).

The standards were prepared in the similar manner to the core samples and were then run after every third sample. Each set of samples was repeated after 4 and 7 days. The measurement of core porewater for each sample took between 60 and 120 s during which time the reading has stabilised. Exact stabilisation time varied for each sample depending on the size of the sample and water content. A stable result was defined by visually flat $\delta^{18}\text{O}/\delta^2\text{H}$ concentration line subsequent to H_2O saturation in the bag reaching 100% relative humidity.

A minimum of 50 values were recorded for each sample and the average, standard deviation and 25th and 75th percentiles plotted. After each reading, the sample was disconnected from the instrument while the LGR sampled atmospheric air for about 200 s to ensure that there was no memory effect resulting from the moisture in the tube or needle. In addition, after about one hour of analysis, the LGR was left to sample atmospheric air for 10 min.

About 10% of 2 L bags were slightly deflated, indicating that minor leakage and therefore isotopic fractionation may have occurred. Based on the H_2O content in the bag remaining within 27,000–30,000 ppm range and ambient vapour content of 9800 ppm, an assumption was made that the vapour loss does not affect the results. Replicate sample analyses (mean difference of 7 samples) indicate reproducibility of results within 0.69‰ $\delta^2\text{H}$ and 0.03‰ $\delta^{18}\text{O}$ uncertainty.

The moisture content in headspace below about 26,000 ppm H_2O was found to severely impact deuterium readings, and range from 27,000 to 32,000 ppm H_2O in the headspace results in more precise reading with an average uncertainty of 0.5‰ $\delta^2\text{H}$. The time required for equilibration is closely linked to the headspace moisture content range, which is dependent on sample moisture content, therefore the lithology and porosity and sample size.

Reported instrument precision of 0.5‰ $\delta^2\text{H}$ and 0.15‰ $\delta^{18}\text{O}$ over 10 s and drift of 0.8‰ $\delta^2\text{H}$ and 0.2‰ $\delta^{18}\text{O}$ over 15 min was minimised by correcting the readings with two secondary $\text{O}^{18}/\delta^2\text{H}$ standards (Los Gatos 2A – 16.14‰ $\delta^{18}\text{O}$ and – 123.6‰ $\delta^2\text{H}$ and 5A – 2.8‰ $\delta^{18}\text{O}$ and

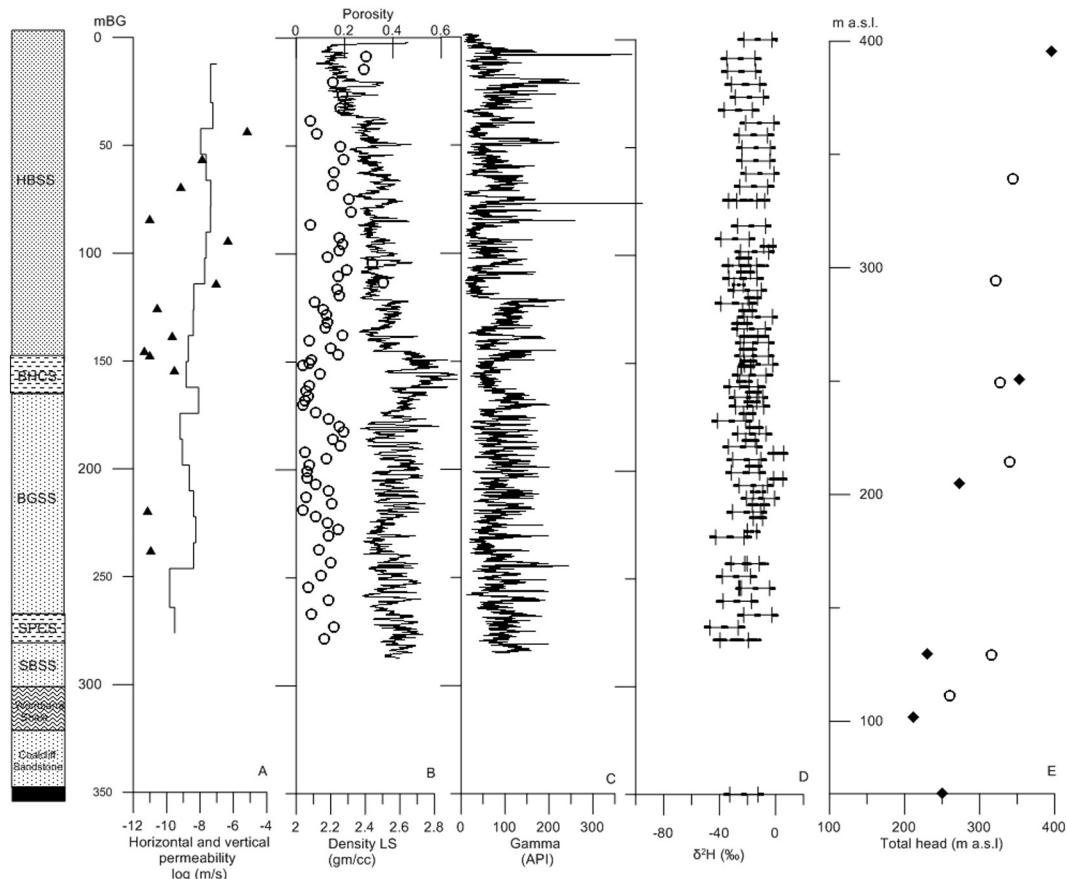


Fig. 2. Horizontal permeability determined by packer tests and vertical permeability determined by Klinkenberg permeability (triangles) (A), porosity determined from moisture content by standard method (open circles) and density geophysical (LS) log (B), gamma downhole log (C), porewater $\delta^2\text{H}$ determined by ICOS as a function of depth-top and bottom samples represent surface and coal seam water respectively (D) and total head distribution from vibrating wire piezometers for S2192 (diamonds April 2013) and S1908 (open circles May 2008) (E).

9.5‰ $\delta^2\text{H}$) and one primary SMOW standard during the analysis. The data set for each sample was corrected for drift by back correction of standards within each set and then applying the same regression analysis to the relevant samples. The uncertainty in isotopic fractionation due to bag deflation is within the instrument reported precision range.

3.2. Geophysical methods and chloride analyses

Geophysical contractor (Weatherford) undertook geophysical bore logging following borehole drilling. The downhole logging suite included density and gamma surveys which were used to compare with the porosity obtained directly from core samples (Fig. 2).

After isotope analysis, each sample was dried in the oven and water content determined based on the standard procedure AS 4133.1.1.1 (2005). This information was used to calculate the porosity and degree of saturation for each sample, and to cross check the validity of the isotope results in particular for samples with low water content.

Samples for chloride analysis were prepared by drying the sample in the oven at 105 °C for 24 h, crushing the sample, diluting with purified MilliQ water (EC 0.05 $\mu\text{S}/\text{cm}$) in 1:5 ratio, mixing for 12 h, centrifuging and filtering the samples. Such prepared samples were analysed for Cl by ICPMS method at UNSW Analytical Centre (Dionex Ics-1000, Autosampler A540). Standards used were 0.4, 2, 4, and 40 mg/L based on the estimated Cl values. Method detection limit for chloride is 0.2 mg/L. Chloride concentration obtained from 1:5 soil suspension was converted to porewater concentration taking into consideration porosity (by multiplying Cl concentration in solution by ratio of solution volume and volume of pores).

3.3. XRF and XRD analyses

Core scanning (using ITRAX multiscanner for scientific scanning of sedimentary cores) XRF spectrometry and optical image and XRD semi-quantitative analyses were performed in the Mark Wainwright Analytical Centre at UNSW Australia on selected samples to characterise the properties of sandstone and claystone cores and to record the variations in elemental composition. The lithology variation and determination of clay component was important in supporting the finding of stable isotope analysis in understanding the groundwater processes. In total 23 core samples (60 mm diameter) varying in length from 5 cm to 15 cm were scanned by ITRAX core scanner. The samples were selected within the 289 m vertical interval and include both samples typical for the unit and samples that exhibited significant heterogeneity.

XRF spectrometry was selected as it is one of the most widely used and versatile instrumental analytical techniques (Baraka-Lokmane et al., 2009). ITRAX scanner provides scans of the core sample along its length using X-ray and optical imaging. Detailed technical information on the instrument is provided in literature (Croudace et al., 2006; Strelti et al., 2004; Tsuji et al., 2004).

A high power X-ray tube, well defined beam (20 × 0.2 mm), and optical RGB line scan camera system provide fast and accurate XRF, radiographic and optical analyses (50 to 200 μm pixel size with 10 cm image width, and true dynamic image range of 9 bits of each colour and 9 bits grey scale). The radiographic image could not be obtained for these core samples as the sample thickness did not allow penetration of X-ray beam. The elemental detection limits are related to the X-ray source

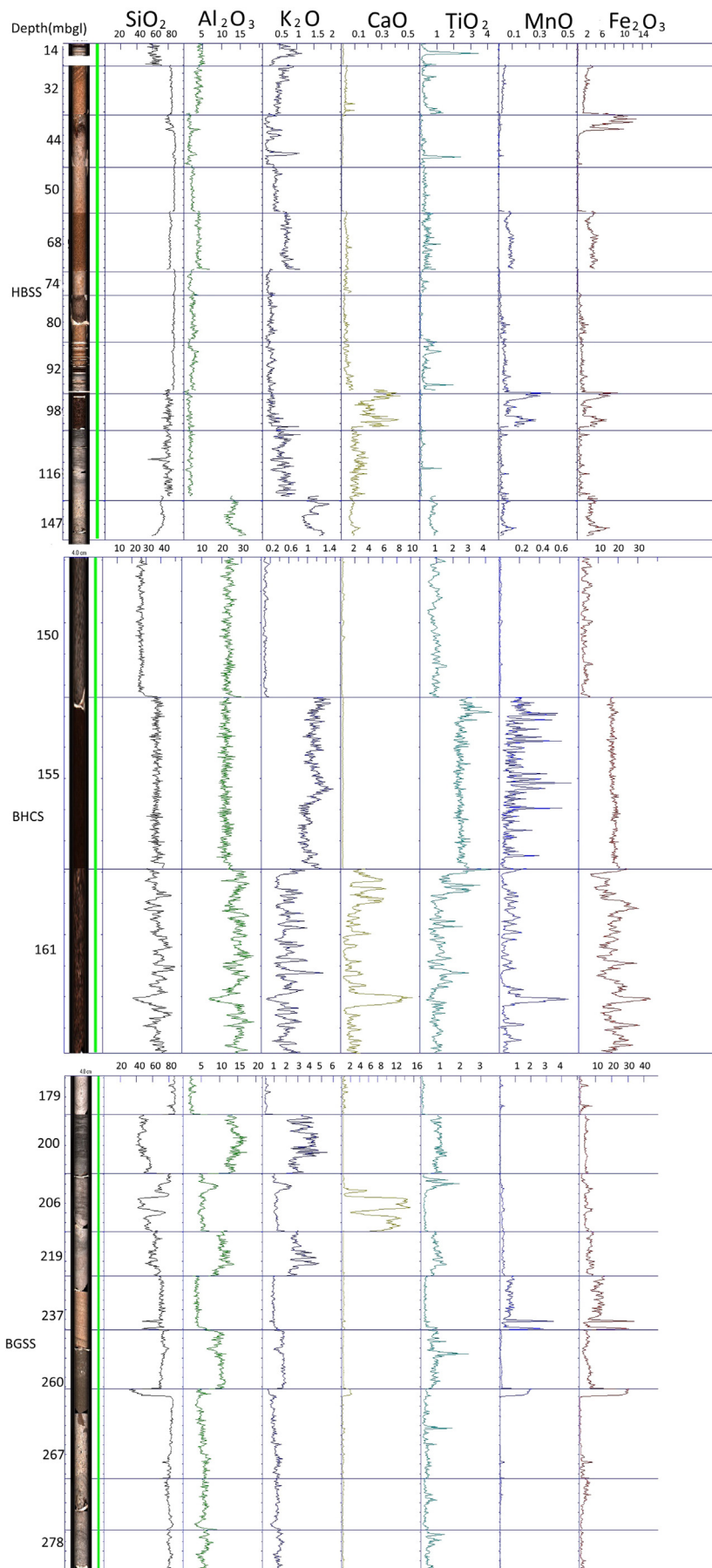


Fig. 3. Calibrated ITRAX scanning results represented as typical element oxides (%) for representative discontinuous HBSS, BHCS and BGSS (top to bottom) (depth not to scale).

that is used (3 kW Mo tube), and the detection of lighter elements can be achieved by using the Cu or Cr tube.

The scanner was operated using the CoreScanner (v8.6.3) software. For XRF measurements, the core scanner moved the sample in 200 μm steps, analysing each step for 15 seconds with good reproducibility, using a Mo (3.1 kW) tube operating at 30 kV and 55 mA. The area analysed at each step was 100 μm x 8 mm. Analysis time is significantly reduced using the core scanner compared with traditional XRF techniques.

The likely elements in the sample were then identified based on analysis of the resultant XRF spectra using the Q-Spec software (v8.6.0) and peak fitting. The major element concentrations were determined based on calibrations (17 samples milled and ground to 70 μm and submitted to the XRF Laboratory, UNSW Australia for analysis on major elements by conventional wavelength dispersive-XRF). These samples were from the same core analysed by the ITRAX core scanner allowing quantitative analysis of elements based on concentrations. The results are reported in weight percentage of oxide element (Fig. 3 and see Supplement).

The XRD analysis was performed on four samples to define mineral composition. XRD analysis is based on the crystal structure rather than optical properties or chemical composition, which is important for clay minerals that are difficult to identify by any other means (Ward et al., 2005). Four samples were selected for analysis based on their high clay content.

3.4. Vibrating wire piezometer data

Pore pressure data was analysed from multilevel vibrating wire piezometers (VWP) installed to monitor change with longwall mine development. VWPs were installed in boreholes S2192 (20 m away from S2220), and S1908 outside of the mined longwall panel respectively (Fig. 1). They were installed in various strata to define the pore pressure distribution and variable vertical gradients between hydrostratigraphic units (Fig. 2). The VWPs were installed in S2192 at around 50 m, 95 m and 140 m below ground (mBG) in HBSS, at 175 mBG and 260 mBG depth in BGSS and in SPCS at 278 mB and in S1908 at 10 and 155 mBG (HBSS) and 201, 276 and 304 mBG (BGSS). The continuous data for S2192 covers the period before the start of Longwall 9 (LW9) extraction in February 2013 until the sensors were disconnected due to subsidence in September 2013 (S2192), and for S1908 May 2008 long before the LW9 was extracted (not whole series shown here). Fig. 2 shows total head distribution at the start of LW9 mining (April 2013 for S2192 and May 2008 for S1908) however with some disturbance at depth due to extraction of previous panels.

Pore pressure data was used to estimate the Peclet number in order to check the overall relative importance of advective versus diffusive transport within the BHCS and BGSS. This non-dimensional number (Bear, 1972) distinguishes between low water velocity ($P_e < 1$) when diffusion dominates and advection is negligible and high velocity where opposite is the case. Peclet number (de Marsily, 1986; Freeze and Cherry, 1979, respectively) is given as:

$$P_e = \frac{v\sqrt{k}}{\omega_0 D_0} = \frac{K \frac{\Delta h}{\Delta z} \sqrt{\frac{\mu K}{\rho g}}}{\omega_0 D_0} \quad (1)$$

$$P_e = \frac{v_e d}{D_e} \quad (2)$$

where v is Darcy velocity (m/day), k is intrinsic permeability (m^2), ω_0 is effective porosity, D_0 is diffusion coefficient and d is average particle diameter.

Two different Peclet number definitions were used as it was found that they lead to diverse Peclet number values (Huysmans and Dassargues, 2003). The intrinsic vertical permeability was obtained

from Klinkenberg permeability on selected core samples by pushing the gas through the sample under confining pressure (South32, 2013). Since Klinkenberg permeability testing uses gas as a media that flows through the sample, it does not allow for any structural void changes during drying prior to testing and geochemical changes during testing, therefore, the results of such testing could overestimate the permeability (Klinkenberg, 1941).

The data from VWP was used to confirm the zones of lower hydraulic conductivity and to understand the vertical hydraulic gradients in order to distinguish between advective and diffusive flow.

In addition, twelve core samples from different units (borehole S2192 drilled at 20 m distance from S2220) were lab tested for vertical permeability by Illawarra Coal at about 20 m intervals starting at 150 m to 289 m depth (Fig. 2). The intrinsic vertical permeability was converted to hydraulic conductivity (assuming fresh water density and viscosity) by multiplying the permeability by water density and gravity and dividing by viscosity. Horizontal permeability was measured along the borehole length by packer testing (SCT, 2012).

4. Results and discussion

4.1. Hydrogeology

The bore log for S2220 indicates that the strata encountered in this drillhole are typical for the southern part of the Sydney Basin (Table 1, Fig. 2). The thickness of HBSS is 145 m, underlain by 142 m of Narrabeen Group and the top of the SPCS was observed at 269 m depth.

Detailed examination of core and gamma geophysical log indicate that within HBSS unit the sandstone beds prevail with thicknesses ranging from 6 m to 50 m, interlayered with occasional 0.01 m to 2 m thick claystone/siltstone bands. Higher degree of heterogeneity is evident within BGSS; the thickness of sandstone beds varies in the range from 2–10 m, with frequent thin (0.01 m to 1 m) siltstone, claystone and conglomerate interbeds.

The piezometric heads in boreholes S2192 (20 m away from S2220) and S1908 (200 m outside of the panel footprint) indicate downward hydraulic gradient and near hydrostatic conditions present in the upper HBSS. The water level in HBSS indicates unconfined conditions. Increase in slope steepness within HBSS indicates an increase in hydraulic conductivity in lower HBSS. This is also supported by vertical hydraulic conductivity measured on core samples.

At the interface with BHCS there is a change to lower hydraulic conductivity with the change in slope direction which coincides with low vertical hydraulic conductivity obtained from core samples (Fig. 2). BGSS shows confinement below low permeability BHCS unit as the head is above the top of the BHCS. Hydraulic conductivity in BGSS is lower than HBSS as evident from the change in total head, with partial depressurisation towards the base of the unit. However, depressurisation at SPCS level and below is a result of development of previous longwall panels in the underlying coal seam (Fig. 2).

An average BHCS vertical hydraulic conductivity of 3×10^{-10} m/s obtained by Klinkenberg permeability testing (Fig. 2). The head in the HBSS and BGSS (immediately above and below the BHCS) at two piezometer elevations suggests downward leakage with head at 323.1, 320.1 m a.s.l. at 249.3, 214.3 m a.s.l., and for S1910 head at 328.33 and 295.04 at 252.20 m and 208.20 m, respectively. The gradient therefore varies from 0.08 and 0.75. The porosity ω_0 calculated from water content was on average 0.03 and the D_0 in water for simple electrolytes is estimated about 10^{-9} m²/s (Appelo and Postma, 2005). The grain diameter was estimated at 0.0025 mm (ISO, 14688–1:2002) Using these constants, the Peclet number for BHCS was calculated as 4.2×10^{-4} to 4.2×10^{-3} using Eq. (1) and 5.8×10^{-6} using Eq. (2). A higher Peclet number was obtained for BGSS using two piezometers installed in this unit, 3.7×10^{-3} , and for HBSS 27 and 0.9.

These numbers are below the upper boundary (<0.5) for advection controlled mass transport (Appelo and Postma, 2005) for BHCS and

BGSS indicating that the concentration profile with depth is mainly diffusion controlled within the claystone and sandstone.

Horizontal permeability measured by packer testing (SCT, 2012) along the length of the borehole points to an overall decrease with depth, however variation can be observed within each unit (Fig. 2). Vertical conductivity is lower than horizontal in all units except in the upper BGSS where they are equal. Relatively high horizontal conductivity drives the advective flow in HBSS and upper BGSS, however in BHCS and lower BGSS the major mass transport is via diffusion as both K_H and K_V are low (below 10^{-9} m/s).

4.2. Porosity and lithology trends

Porosity calculated from measured water content on preserved core samples varies from 0.02 to 0.32 over the full sedimentary sequence. While the plotted results show a tendency of decrease in porosity with depth, the porosity was more sensitive to lithology (Fig. 2).

The top 41 m of HBSS unit has lower density (2.2 g/cm³) compared to the lower HBSS, most likely as a result of surface weathering. This is supported by gamma log which indicates that sandstone matrix may have minor clay component. Below this depth density (LS) increases to around 2.4 g/cm³ and then remains stable to the base of the unit. The lithology log indicated that the HBSS was relatively massive and homogenous, however the gamma log does not support this interpretation based on the presence of numerous thin (0.1–0.5 m) clay rich bands and with higher presence of clay matrix in sandstone.

A sharp interface is evident at the contact with BHCS, with decrease in porosity and an increase in gamma indicating an increase in clay content with transition to siltstone. BGSS appears to form two zones; the upper 30 m thick heterogeneous unit where density decreases with depth, and lower unit below 200 mBG where there is no trend with density with depth. Higher density in the upper BGSS is a result of frequent conglomerate interbeds with clay matrix

4.3. Elemental and geochemical characterisation of sandstones and claystones

The geochemical concentrations obtained by XRF and XRD analyses (Fig. 3) and (further information in the Supplement) were correlated using the sandstone classification system applicable for terrigenous sands and shales (which includes claystone and siltstone). The scheme developed by Herron (1988) uses $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3/\text{K}_2\text{O}$ ratios and Ca concentrations to characterise the lithological units and allows the distinction between quartz rich and clay rich samples. HBSS samples are typically arenite and subarkose, while BHCS plots in the shale area (Fig. 4). Based on the XRD results, which provide semi-quantitative analysis, BHCS has high likelihood of kaolinite, siderite and haematite

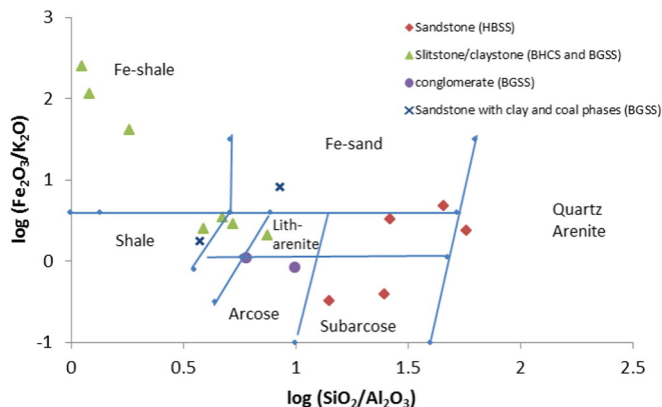


Fig. 4. The classification of selected representative sedimentary rock core samples based on clay, feldspar and quartz content, and mineral stability indicating rock maturity (after Herron, 1988).

occurrence (Table 2). Kaolinite is formed in humid and warm environments, and as a result, the formation of these clays is associated with diluted porewaters and low ionic concentrations (Morad, 2003; Worden, 2003). BGSS has high probability of both quartz and kaolinite present, and the calibrated ITRAX XRF results point out the significant heterogeneity with varying range of SiO_2 , Al_2O_3 and K_2O in the vertical profile.

The results from weathering intensity diagram confirm the advanced weathering trend and types of clays present in core samples have composition similar to illite and kaolinite, which is consistent with the XRD results, geophysical log interpretation, porosity and existing (Pells, 1993) literature.

4.4. Analysis of water-vapour stable isotopic composition and chloride

4.4.1. Water-vapour stable isotopic composition

The isotope results obtained by the porewater analysis of vapours were expressed as water using the fractionation factor (Majoube, 1971) between water and vapour at 25 °C (the lab temperature was 24 °C). The drilling water sampled within 24 h from spiking with deuterium oxide, has $\delta^2\text{H}$ composition significantly more enriched compared to porewater composition ($+9.1$ to $+313.6\%$ VSMOW), while at the same time the porewater composition remained within the similar range as before the addition of deuterium oxide. This indicates that core was not contaminated during drilling.

The standard isotope results were plotted and the regression equation used to correct the raw sample isotope values. Overall, the $\delta^{18}\text{O}$ results vary from -9.5% to 2.8% and $\delta^2\text{H}$ from -41.9% to 7.9% (Fig. 5). The error bars shown represent the uncertainty in both the analytical method and instrument drift correction. The standard deviation being the result of analytical uncertainty ranges from 0.23 to 1.05% for $\delta^{18}\text{O}$ and 0.29 to 3.75% for $\delta^2\text{H}$. The uncertainty arising from the drift correction varies for $\delta^{18}\text{O}$ from 1.2% for even samples to 0.5% for odd samples (Fig. 5). The difference in uncertainty in drift correction is a result of initial analysis undertaken on even numbered samples, followed by odd numbered samples. The latter analysis has lower uncertainty due to improved laboratory control of samples and standards including the bench holding time, and constant temperature during measurement. The majority of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ data from core porewater, mean weighted rainfall average from Lucas Heights station, surface water and the mined coal seam water plot on or close to local (Sydney Basin) weighted meteoric water line (Hughes and Crawford, 2013) as shown on Fig. 5. The standard deviation of the mean of the porewater samples for $\delta^{18}\text{O}$ is 1.3% and for $\delta^2\text{H}$ 8.03% . Considering some evaporation of porewater over time, the standard deviation excludes the samples which show negative or low D-excess values. There is a significant advantage in comparing the porewater results to weighted LMWL as it provides the weighted monthly $\delta^{18}\text{O}$ and $\delta^2\text{H}$ data to most significant local precipitation events. These results show that the groundwater is recharged under environmental conditions similar to modern rainfall resulting in wide variability in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (Fig. 6). This is due to, primarily, impact of the ECL and western trough weather systems, but also due to evaporation. The ECL system occurred more frequently in winter, while the western trough ($\delta^{18}\text{O}$ 1% to -12%) was more frequent in spring and summer. The precipitation weighted $\delta^{18}\text{O}$ for ECL is -11% (min of -26% , max -4% and standard deviation 5.65%) and for westerly inland trough -6.13% (min of -12% to 2% , standard deviation 3.03%). The study by Crawford et al. (2013) found that the synoptic conditions were the important factor in determining the variability of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in rainfall, and the variability was the result of the prevailing weather systems, especially the impact of ECL system vs. the westerly systems, and the distance from the ECL centre. This was considered to have the impact on long term trends of isotopic signal in the Sydney Basin. We note that the variation in the rainfall isotopic signal and standard deviation from the measured values of both ECL and westerly trough is significantly greater than that of the observed porewaters. In addition to

Table 2
XRD results for Bald Hill Claystone and Bulgo Sandstone.

Sample	Formation	Minerals present in decreasing likelihood order					
9	Bald Hill Claystone	Siderite	Quartz	Hematite	Kaolinite-1A		
36	Bald Hill Claystone	Hematite	Kaolinite-1A	Hydroxylapatite (Ca Apatite)			
14	Bulgo Sandstone	Quartz	Kaolinite-1A	Siderite	Anatase	Muscovite-2M1	
18	Bulgo Sandstone	Quartz	Siderite	Muscovite-2M1	Kaolinite	Mica	

variability due to synoptic conditions, a number of HBSS samples are indicative of evaporative enrichment. Therefore, the historical variability seen in porewater $\delta^{18}\text{O}$ and $\delta^2\text{H}$ is the result of a combination of long term impact ECL and westerly weather systems and evaporation at surface. The range of obtained $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values is narrower than that reported in GAB (Harrington et al, 2013).

Surface water sample is slightly enriched both in $\delta^{18}\text{O}$ and $\delta^2\text{H}$, with low D-excess which is indicative of evaporation.

D-excess average for all samples is 13.5‰, similar to weighted average D-excess in precipitation in the Sydney Basin (17.09‰ with standard deviation of 3.15‰ for ECL and 16.03‰ with standard deviation of 3.71) documented in Hughes and Crawford (2013). High D-excess is a result of the proximity to the ocean, sea surface temperature, evaporation and low humidity.

Based on the stable isotope composition and supported by other investigative methods four different zones are distinguished.

4.4.2. HBSS – Zone 1

The depth profiles show variation in the HBSS both in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ with a close to linear trend with depth (Fig. 6). Based on the stable isotope composition, lithology, porosity and groundwater pressure HBSS is considered to be one zone (Zone 1)

In temperate climate with distinctly dry (hot) summers (Sydney Basin), similar to semi-arid zones (Peel et al., 2007), the evaporation process in shallow partially saturated zone can result in isotopic water enrichment (Nativ et al., 1995; DePaolo et al., 2004; Cuthbert et al., 2014). However, due to limited water saturation, the volumetric water loss due to evaporation, and following volumetrically larger rainfall, this zone will typically experience negligible isotopic enrichment (Allison, 1982; Cuthbert et al., 2014) unless there is a near surface or surface store of water which can be a source of isotopically enriched recharge waters.

A linear weighted regression of porewater samples in the HBSS below 80 m depth has a slope of 2.6 ± 1.2 indicating an evaporative isotopic enrichment of some samples. Weighted regression was not plotted for samples to 80 m depth, as the correlation was insignificant and dataset was relatively small. Given the groundwater age within 3–6 ka (KBR, 2008) and up to 14 ka as reported by Bartrop (2014), the isotopic enrichment may have occurred in a wetter period with temperatures similar to current (Fitzsimmons and Barrows, 2010). In the Sydney Basin, there has been no glaciation since the Permian (Mii et al., 2012) however there is evidence that climate was cool to cold with temperatures $6\text{ }^\circ\text{C}$ to $10\text{ }^\circ\text{C}$ during late Pleistocene (18–20 ka) and temperature during Holocene slightly higher ($1\text{ }^\circ\text{C}$) but generally similar to today's (Kershaw et al., 2000; Herbert, 2001). During wetter period more standing water (which would support the evaporitic enrichment) would have been present across southeast Australia (Fitzsimmons and Barrows, 2010) and within the southern Sydney basin where no significant change to landscape occurred during Holocene. This is further confirmed by a climate study by Fitzsimmons and Barrows (2010) which indicates higher rainfall (25%) during the early to mid-Holocene in semi-arid and temperate SE Australia between 10 and 4.5 ka, and drier conditions over the last 3 ka. It is hypothesised that this change in humidity may have resulted in groundwater $\delta^{18}\text{O}$ variations that could be used to better define the hydrogeology of the Basin. Yet, increased moisture conditions during Holocene may not have lasted long enough (approximately 6 ka) for groundwater flow and diffusion to smooth temporal variations.

Significant vertical variability in isotope composition in HBSS is also likely due to the horizontal bedding and layered stratification from laminated (0.01 m) to thickly bedded (0.3–1 m) (Anonymous, 1971), where the primarily advective mass transport occurs along the horizontal bedding planes. The variability in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ is also supported by the synoptic weather conditions and the presence of ECL and westerly

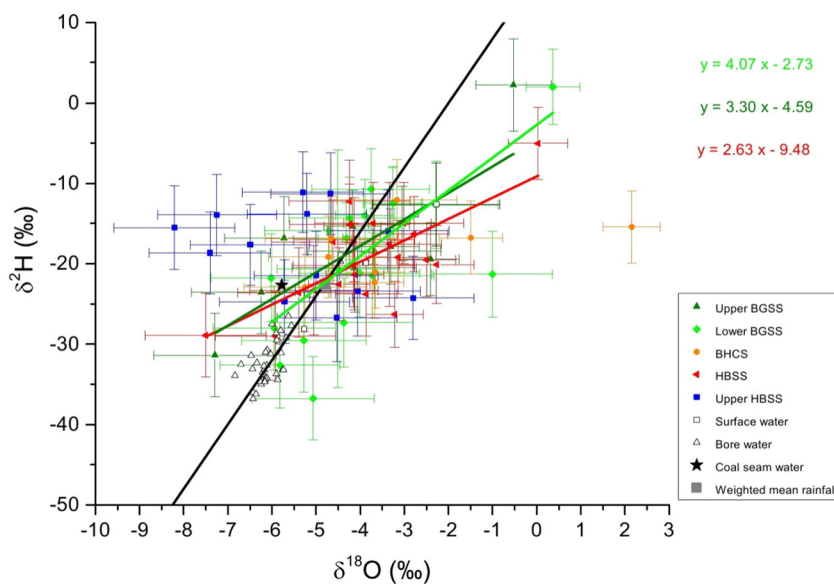


Fig. 5. $\delta^{18}\text{O}$ and $\delta^2\text{H}$ porewater analysis and Sydney precipitation weighted LMWL (thin grey line) (Hughes and Crawford, 2013) obtained from monthly average weighting of $\delta^{18}\text{O}$ and $\delta^2\text{H}$, data from other studies in the Sydney Basin are presented for comparison. Linear weighted regression lines (weight is given as $1/\text{error}^2$) are shown for datasets where there was good correlation (colour coded to correspond with hydrostratigraphic units).

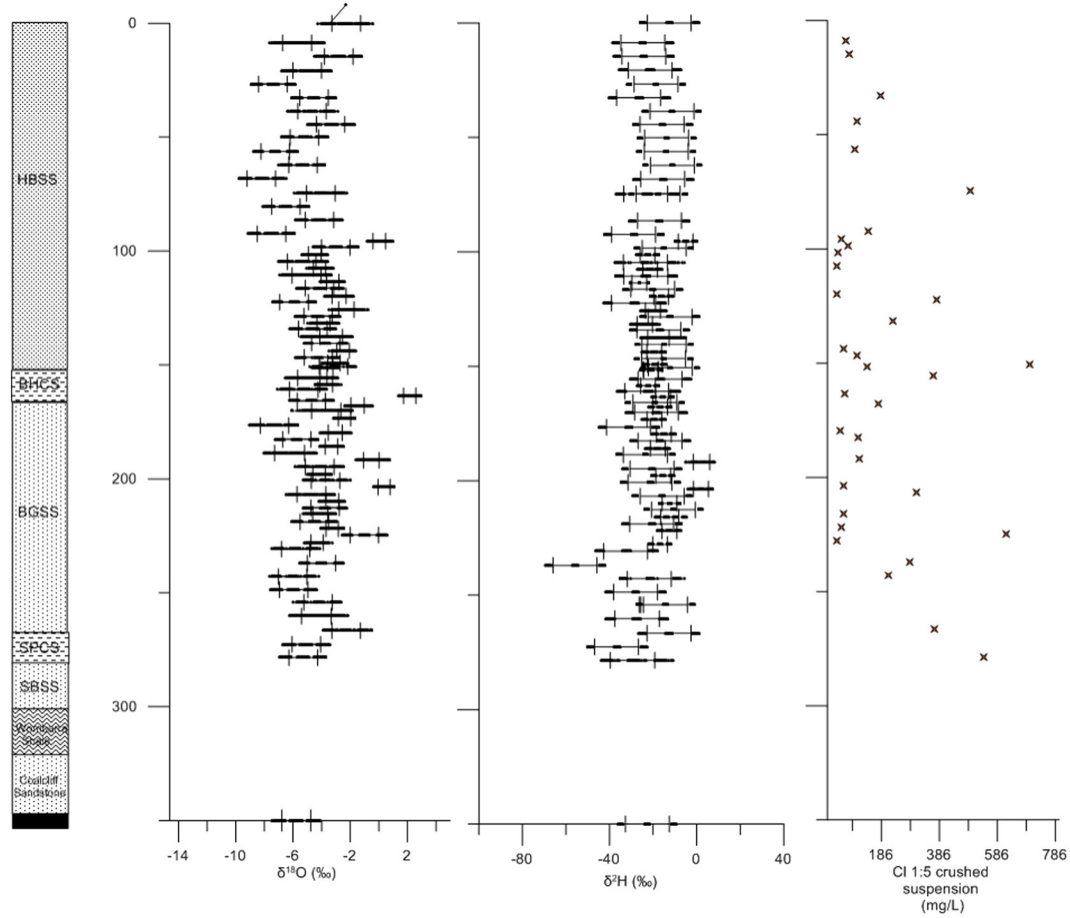


Fig. 6. Porewater $\delta^{18}\text{O}$ and $\delta^2\text{H}$ determined by ICOS and Cl determined by 1:5 crushed rock suspension.

precipitation systems as found by Crawford et al. (2013). The influence of heterogeneity becomes more significant with depth as is confirmed by variation in chloride concentration (Fig. 6). The hydraulic conductivity within discrete HBSS layers varies depending on the proportion of silt, clay and organic component in the matrix and porosity of the material, therefore the flow, mass transport and mixing between isotopically modern and old waters will vary accordingly. The most positive $\delta^2\text{H}$ values ($> -10\%$) are associated with clean grey coarse-grained sandstone, while the most negative values ($< -25\%$) are associated with layered, yellow, medium grained, and occasionally ferruginised sandstone. A possible explanation for this difference maybe that ferruginised sandstone had higher porosity, before cementation occurred. The isotopic composition of sandstone layers that contain haematite and goethite is similar to modern day rainfall.

Although in general chloride concentration increases with depth, there was no correlation with water isotopes and the relationship is statistically not significant with low R^2 . It is therefore likely that different processes dominate the change in Cl concentration when compared to stable isotopes. There are several possible factors that may contribute to this: weathering, sorption or dry deposition. The Cl ion is considered conservative and since it is negatively charged it will not be sorbed onto clays. However, Al- or Mg-rich illite has been found to show positive adsorption of chloride ions that is due to hydrolysis (Edwards et al., 1965). In HBSS illite occurs as cementing material in pores (up to 18%) and the variations in its percentage will depend on source area of weathering (Zaid and Al Gahtani, 2015). The other possibility is dry deposition from marine aerosols given the proximity to the ocean. Inspection of core data did not reveal any further information to support either hypothesis.

4.4.3. BHCS – Zone 2

The range in $\delta^{18}\text{O}$ values in the BHCS is smaller compared to the range in HBSS values (Figs. 2 and 6). On the contact with low permeability BHCS, there is a change to more negative values (at 150 m), for both $\delta^{18}\text{O}$ and $\delta^2\text{H}$. BHCS porewater samples plot on a regression line with a correlation of 0.49. This correlation is not considered significant and a low regression slope (slope of 0.7 not presented here) is practically impossible to detect in evaporation experiments (Gonfiantini, 1986). The BHCS average $\delta^{18}\text{O}$ values (with negligible standard deviation) are more positive than the modern weighted average; however, this is due to the variation in input rainfall signal, rather than evaporation.

Porewater chloride within BHCS reaches a concentration of 700 mg/L (Fig. 6), and an increase along the HBSS boundary from 100 to 700 mg/L is significant. The correlation between stable isotope and Cl concentration is not significant. The change in Cl is likely to be reduced by sorption onto Al and Mg-illite which is present in intragranular pore spaces (Al Gahtani, 2013). Towards the bottom of this unit, density decreases, porosity increases and gamma is higher, which indicates tighter material packing and higher clay content.

4.4.4. BGSS – Zones 3 and 4

Within the underlying BGSS the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values remain stable near the top of this unit (top 30 m) but become more negative with depth with $\delta^2\text{H}$ values shifting from about -10% to -30% . BGSS can be separated in two zones (Zones 3 and 4) based on the stable isotope porewater composition, groundwater flow characteristics (permeability), porosity and Cl concentration.

The $\delta^{18}\text{O}$ mean of porewater samples within the upper Zone 3 (top 30 m) are both more positive and more negative than the

average weighted rainfall, however below 200 m depth (zone 4) the $\delta^{18}\text{O}$ mean of groundwater is more positive than average weighted rainfall.

The BGSS samples have slope of the linear regression of 3.92 ($R^2 = 0.6$), and the 95% confidence limit on the regression line has standard deviation of the slope 3.9 ± 1.2 (for degree of freedom >6) and intercept of -2.9 ± 5.8 . The slope of regression was 3.3 and 4.07 respectively for the upper BGSS and lower BGSS. A study by KBR (2008) at a location 25 km to the southwest, found that the groundwater at this depth was over 6000 years old and that the age was increasing with depth. During the period between 8000 to 6000 years relatively drier conditions prevailed compared to the early Holocene (Singh et al., 1981) and the slope of 4.6 suggests relatively low humidity (<50%) (Gonfiantini, 1986). The isotopic signature of the sample from nearby surface water (end member) indicates strong evaporitic enrichment and plots just below the BGSS regression line. This suggests that groundwater carries both the past signature of low humidity climate conditions with further enrichment from surface water.

There was a weak relationship between Cl and stable isotopes, similar to upper units, suggesting that the Cl source was not evaporation related. Within BGSS the porewater concentrations in Zone 3 are around 100 mg/L with an increase with depth in Zone 4 to about 600 mg/L. A possible explanation for the relatively low Cl concentrations in Zone 3 might be that recharge occurs laterally where BGSS outcrops at a distance several kilometres from site and the presence of higher permeability thin interlayers and dissolved lithic grains (Al Gahtani, 2013), as determined by ITRAX XRF scanning and density log, enable preferential groundwater flow and advective mass transport.

The progressive change in lithology, with high variation confirmed by XRF and density log (Figs. 2 and 3), results in variable characteristics. The intergranular spaces tend to be filled with illite, or illite occurs as coating on the detrital grains, and due to its adsorption capacity it can change Cl concentration in groundwater. The fact that it occurs sporadically (Bai and Keene, 1996), although it is second most common clay mineral, is consistent with Cl concentration that varies independently of density, porosity or stable isotope data.

Within the Zone 4, a trend towards stable isotope depletion is noticeable with depth. As the siltstone component and bed thickness increases, the hydraulic conductivity decreases and the diffusive transport becomes more important. Detailed lithology review, Cl concentrations and mineralogy confirm this hypothesis (Figs. 2 and 3).

At the bottom of BGSS and top of SPCS, the increase in Cl concentration and depletion in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ may be a result of upward diffusion from the Sydney Subgroup (top of Illawarra Coal Measures) which was deposited in fluvial to shallow marine environment. This is supported by the fact that Permian coal measures and the underlying Shoalhaven Group has been reported as saline at this and other locations throughout

the southern part of the Basin (Merrick and Akhter, 2013; Sherwin and Holmes, 1986).

4.5. Conceptual model validation

Simple analytical cross validation of the discussed conceptual model used both estimate of advective and diffusive flow. A couple of hypotheses were tested using $\delta^{18}\text{O}$ to see if the input signal after fractionation, advection and mixing can reproduce the range of values observed in porewater samples. Firstly, a hypothesis was tested to see if the majority of initial rainfall variability (considering ECL and western trough events) is transmitted to groundwater system given that the porewater stable isotope results were suggesting this. Secondly, is it possible that the observed $\delta^{18}\text{O}$ is a result of diffusion, and if so what are the possible mixing scenarios that could produce the observed value? A full range of rainfall (ECL and western trough events) and surface water (site specific and from other studies in the Basin) $\delta^{18}\text{O}$ data (endpoint) were used to simulate diffusion and mixing to quantify the isotopic composition during these processes (Table 3). Mixing of rainfall and creek water in different ratios, indicated that 90:10 ratio includes the range of groundwater $\delta^{18}\text{O}$ results determined on porewaters. Diffusion through BHCS over a period of 3000 years was required to match the observed stable isotope value. This was achieved using a range of average monthly rainfall as an input applying Fick's law. Diffuse recharge was subsequently mixed with different ratios of rainfall and creek water that flows horizontally through interbeds (Q_h) to Zones 1 and 3. The results (Table 3) indicate that advective flow velocity through HBSS and upper BGSS is within the results obtained by other studies in the Basin (Bartrop, 2014). Diffuse recharge to rainfall-surface water (90:10 ratio) mix in a 10:90 ratio provides the $\delta^{18}\text{O}$ range that is observed in BGSS porewater and supports the conceptual model. The mixing outcome is not related to any particular depth but explains equal mixing at any point in the depth profile. The use of simple analytical model is considered appropriate in this case as it considers the stable water isotopes. However, where radioactive tracers are available or input and output time series data for stable isotopes of water, a lumped parameter model should be used (Jódar et al., 2014; Maloszewski et al., 1983).

Overall the ICOS method applied to analyse porewater isotopic composition from core samples has great advantage as it provides detailed vertical depth profile. It is particularly useful in mining environments where due to strata movement the standpipe piezometers generally fail. In addition, sampling from depths below 200 m is challenging and a dense network of piezometers is required to be able to sample from discrete zones. The analysis of porewaters is relatively quick, and the interpretation depends on good sample preservation. When combined with other traditional hydrogeology methods it can provide detailed information on groundwater systems. In the mining environment, the

Table 3
Advective and diffusive flux and mixing of waters for conceptual model validation.

	Unit	Velocity (m/s)	$\Delta^{18}\text{O}$ (‰) SMWL	Time (years per unit)
Precipitation (end member)			-26 to 3	
Creek (end member)			-5.2 to -2.27	
Porewater/groundwater			-9.5 to 2.8	
Advective flow (vertical)	HBSS	0.038		14
	BGSS	1.7×10^{-5}		15,000
Diffusive flux	BHCS		-4.1	3,000
Mixing	Ratio			
Rainfall: creek water	90:10		-23.9 to 2.5	
	80:20		-21.8 to 1.9	
Diffusive recharge: creek water	20:80		-5.03 to -2.54	
	30:70		-4.92 to -2.82	
Diffusive recharge: rainfall	15:85		-22.7 to 1.9	
	50:50		-15.05 to 0.55	
Diffusive recharge: rainfall-surface water	10:90		-21.6 to 1.8	
	40:60		-15.8 to 0.15	

knowledge of performance of such systems is important for the protection of surface water and related ecosystems.

5. Conclusions

This first porewater stable isotope $\delta^{18}\text{O}$ and $\delta^2\text{H}$ study on rock cores from the Sydney Basin has identified four distinctive hydrogeological zones and evidence for recharge and groundwater flow within thick sedimentary strata. The importance of thin low permeability units is recognised based on the mineralogy and density. Measured variability in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ is primarily due to an input rainfall signal (synoptic weather conditions) followed by evaporation processes. This is confirmed by simple analytical mixing model which is considered suitable given that stable isotopes of water are analysed. Identification and characterisation of these zones is important in order to understand the level of protection required to maintain the sensitive ecosystems (wetlands) above the underground coal mines.

Zone 1 coincides with HBSS unit where horizontal flow (Q_h) is greater than vertical flow (Q_v), based on permeability and gradient, and the mass transport occurs mainly by advection. Zone 2 is represented by BHCS where both Q_h and Q_v are low and mass transport occurs by diffusion. Zone 3 is equivalent to the upper BGSS, with mass transport occurring primarily by advection (based on permeability and gradient) with lateral recharge to more permeable beds at the outcrop, and Q_h equal to Q_v . Zone 4 (lower BGSS and upper SPCS) is distinctly different with Q_v smaller than Q_h , but with lower porosity, and head distribution showing decrease in permeability compared to Zone 3.

Porewater is of meteoric origin, plotting close to LMWL but with lower gradient, indicative of evaporitic enrichment of the source water. The variability is due to past climate conditions and the strong presence of ECL and western trough weather systems.

In terms of lithology, HBSS (Zone 1) was found to be more homogeneous compared to BGSS. Contrary to expectations, the study did not identify a link between Cl and stable isotope data. Cl concentration is relatively low (<500 mg/L) and although conservative, it is likely that its source is not of evaporitic origin, but is due to porewater rock interaction and adsorption onto Al and Mg-illite. This hydrostratigraphic zone is unconfined, hydraulic conductivity is relatively high (3.3×10^{-8} m/s) therefore mass transport occurs by advection.

The BHCS (Zone 2) is a distinct hydrogeological zone, as evidenced by change in head, porosity, ITRAX and density results. Although mostly linear vertical trend, a slightly negative shift in $\delta^2\text{H}$ and $\delta^{18}\text{O}$ occurs at the boundary with the overlying HBSS. The average $\delta^{18}\text{O}$ of groundwater is highly influenced by the western inland trough. The mass transport through this layer is dominated by diffusion, with a significant change observed in lithology, clay content and density/porosity compared to Zone 1. Kaolinite, siderite, illite and iron rich minerals are present; however, there are no swelling type clays. Their presence confirms the humid and warm environment depositional environment (with porewaters diluted) and therefore correlates with the low Cl content. The permeability is significantly lower in this unit as confirmed by change in the pore pressure slope and direct testing of core samples.

Within BGSS and top of SPCS (Zones 3 and 4) the depth profiles indicate significant strata heterogeneity (0.1 to 2 m thick interbeds). Variation in stable isotope results was attributed to significant long term variation in rainfall recharge $\delta^{18}\text{O}$ as a result of strong influence of synoptic weather ECL and westerly system in the Sydney Basin area but also due to evaporation.

Consistent with low Cl concentration is the fact that only diluted porewaters provide favourable conditions for deposition of kaolinite found in BHCS and BGSS units. The presence of Al and Mg-illite influences the variability in Cl concentration due to adsorption capacity. The porewater is of meteoric origin, showing evaporitic enrichment and plotting close to surface water sample.

Diffusion is considered to be the main driver of solute mass transport in this zone mainly due to presence of thicker (0.3 to 1 m) claystone and siltstone units and presence of thin to medium siltstone and claystone interbeds (<0.3 m) in particular at the bottom of the section within the upper SPCS (Fig. 2). In addition, higher presence of carbonate cement, clays and overgrowth on the quartz grains reduces porosity. The negative trend is most likely the result of upward diffusion from the underlying Illawarra Coal Measures, with the opposite trend observed in Cl concentration. This hypothesis is supported by the marine character of the underlying strata.

The findings have confirmed the main hypothesis and demonstrated that $\delta^{18}\text{O}$ and $\delta^2\text{H}$ porewater equilibration on core samples can be used in combination with other supporting methods to delineate groundwater processes in the sedimentary strata in highly heterogeneous strata. This finding has an implication on the level of protection required to preserve the health of the ecosystems in the areas above the extraction of longwall panels. However, this level of detail can only be achieved if detailed vertical profiles are available. We show that, the advective transport is the main driver in Zones 1 and 3, while transport by diffusion (Zones 2 and 4) is manifested with a change in stable isotope composition change in slope in pressure head with depth, porosity, low permeability and mineralogical composition.

We demonstrate that the ICOS isotope method can be applied to heterogeneous study of regional basins with the support of other investigative methods provides valuable information to understand heterogeneous stratified groundwater systems.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2015.08.075>.

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